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Relations Among Various Dissolved Substances in the Big Falls Headpond, Mersey River, Nova Scotia

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ABSTRACT

Farmer, G.J. and D. Ashfield. 1990. Relations among various dissolved substances in the Big Falls headpond, Mersey River, Nova Scotia. Can. Tech. Rep. Fish. Aquat. Sci. No. 1755. v + 11 p.

Water samples were collected at various depths of the Big Falls headpond during and after the period of thermal stratification to determine the relations among a number of dissolved substances. The headpond was thermally stratified during the May-August period when dissolved oxygen concentration decreased near the bottom and free carbon dioxide concentration increased. Oxygen concentration near the bottom declined to 1.7 mg/L by 22 August and free carbon dioxide concentration increased to 11.2 mg/L. These changes in oxygen and carbon dioxide concentrations near the bottom of the headpond were accompanied by increases in apparent colour and in total iron which reached a concentration of 1520 µg/L on 22 August. Concentrations of manganese and aluminum near the bottom did not change during the period of thermal stratification. The headpond cooled during September and thermal stratification was no longer evident. This allowed circulation within the headpond, resulting in an increase in the concentration of dissolved oxygen near the bottom and decreases in the concentrations of free carbon dioxide and total iron. The iron cycle within the Big Falls headpond is discussed as well as the consequences of using hypolimnetic water containing elevated concentrations of iron for fish culture purposes.

Key words: Atlantic salmon, salmon culture, dissolved oxygen, free carbon dioxide, iron, manganese, aluminum.

RÉSUMÉ

Farmer, G.J. and D. Ashfield. 1990. Relations among various dissolved substances in the Big Falls headpond, Mersey River, Nova Scotia. Can. Tech. Rep. Fish. Aquat. Sci. No. 1755. v + 11 p.

On a recueilli des échantillons d'eau à diverses profondeurs du bassin d'amont des chutes Big, durant et après la période de stratification thermique, dans le but d'établir les rapports existants entre diverses substances dissoutes dans cette eau. La stratification thermique du lac a eu lieu durant la période mai-août, alors que les concentrations d'oxygène dissous ont diminué près du fond et que les concentrations d'oxyde de carbone libre ont augmenté. Au 22 août, les concentrations d'oxygène à proximité du fond étaient tombées à 1,7 mg/l et celles d'oxyde de carbone libre montées à 11,2 mg/l. Ces changements de concentration près du fond du bassin d'amont se sont accompagnés d'une intensification de la couleur apparente et d'un accroissement de la teneur en fer, qui, au 22 août, s'établissait à 1520 µg/l. Les concentrations de manganèse et d'aluminium près du fond n'ont pas changé durant la période de stratification thermique. Le bassin d'amont s'est rafraîchi durant septembre, occasionnant une disparition de la stratification thermique et une circulation qui a eu pour effet de faire accroître la concentration d'oxygène dissous près du fond et de réduire la concentration d'oxyde de carbone libre et la teneur en fer. On discute également ici du cycle du fer dans le bassin d'amont ainsi que des conséquences de l'emploi d'eau hyplimnique à forte teneur en fer pour la pisciculture.

Mots clés : saumon de l'Atlantique, pisciculture du saumon, oxygène dissous, oxyde de carbone libre, fer, manganèse, aluminium.

INTRODUCTION

The Mersey Fish Culture Station is located on the Mersey River which drains to the southwest coast of Nova Scotia. The station has 7.6 and 11 m Swedish-type ponds and an annual production of 300,000 one-year-old Atlantic salmon (Salmo salar) smolts. A series of dams have been constructed on the river for hydroelectric purposes. Water is withdrawn from the Big Falls headpond by means of dual 60 cm diameter polyethylene intakes and delivered to the station in a 30 cm diameter polyethylene pipeline. One of the intakes is located at a water depth of 2 m and the other on the bottom of the headpond at a depth of about 8 m. Because the headpond surface temperature ranges from 22-27°C during the summer, cooler water is withdrawn from a depth of 8 m and provided to the salmon from mid-June to early September.

Like a number of rivers which drain to the Atlantic coast of Nova Scotia, the Mersey River is acidic, dark brown in colour, lacks acid-neutralizing capacity, has a low calcium concentration and an elevated concentration of total dissolved aluminum (Farmer et al. 1980, 1989a). Organic, rather than inorganic aluminum is the dominant form of aluminum in acidic, brown-coloured, Nova Scotia rivers and high hydrogen ion concentration is the primary lethal factor (Lacroix and Townsend 1987). Because of the acidity of the Mersey River, water supplied to salmon at the station is first treated with limestone gravel ($CaCO_3$) to alter pH and calcium concentration.

A mortality of 8.6% occurred among the 683,340 juvenile Atlantic salmon at the station during the 12-25 August 1988 period (Farmer et al. 1989b). The salmon parr had been provided with water withdrawn from the bottom of the Big Falls headpond. The water smelled of hydrogen sulphide, had a dissolved oxygen concentration of 0.2 mg/L, a total iron concentration of 4405 µg/L and an apparent colour of 220 relative units. Aeration of the hypolimnetic water as it entered the salmon rearing ponds resulted in the formation of a reddish-brown precipitate which was observed to accumulate between the secondary lamellae of moribund parr. Farmer et al. (1989b) suggested that conditions near the bottom of the headpond favoured the reduction of ferric hydroxide found in the bottom sediments and the release of ferrous bicarbonate which is soluble. Subsequent aeration of water containing ferrous bicarbonate at the rearing ponds resulted in the formation of ferric hydroxide according to the equation:

$$4\ Fe(HCO_3)_2 + 2\ H_2O + O_2 = 4\ Fe(OH)_3 + 8\ CO_2$$

Ferric hydroxide is an insoluble precipitate which appeared to adhere to the gill tissue of the salmon parr resulting in an impairment of their respiratory function (Farmer et al. 1989b).

To better understand the relations among a number of dissolved substances in the Big Falls headpond, water samples were collected from various depths on six occasions during the 23 May - 22 October 1989 period. Of special interest were the development and subsequent breakdown of thermal stratification, the relations among concentrations of dissolved oxygen, free carbon dioxide and total iron, and determining the concentrations of other potentially toxic substances such as manganese, aluminum, total ammonia, hydrogen sulphide and hydrogen ions.

MATERIALS AND METHODS

Water samples were collected from the Big Falls headpond in the area of the hatchery intakes at depth intervals of 1 m on six occasions during the 23 May - 22 October 1989 period using a Kemmerer water sampling bottle. Water for the determination of pH and apparent colour was transported to the laboratory in 250-ml polyethylene containers which had been washed with

laboratory detergent and then rinsed with deionized water. Apparent colour was measured with a Helige Aqua Tester and pH within 24 h using a Metrohm Herisau pH meter. Water for determining total manganese, iron and aluminum concentrations was stored in 250-ml polyethylene containers which had been washed in a 50% HNO_3 solution and then rinsed with deionized water. Each sample was preserved by adding 1-ml of 50% HNO_3 solution and the metal concentrations determined at a later date by use of an emission spectrophotometer (Jarrel-Ash, AtomComp).

Water samples for determining concentrations of total ammonia were stored in washed, 500-ml polyethylene containers and preserved by adding 1-ml of 50% H_2SO_4 solution. Total ammonia concentrations were determined in the laboratory using an Orion model 95-10 ammonia electrode and a Fisher Accumet model 230 pH/ion meter (APHA-AWWA-WPCF 1980). Water for determining free carbon dioxide concentrations was stored in washed, tightly-sealed, 1-L polyethylene bottles. Free carbon dioxide concentrations were determined the day of sampling by titration to pH end point 8.3 using 0.0454N Na_2CO_3 (APHA-AWWA-WPCF 1980). Temperatures and dissolved oxygen concentrations were determined at various depths of the headpond with a YSI oxygen meter equipped with a 15 m cable and submersible stirrer.

RESULTS

Temperature of the Big Falls headpond in the area of the hatchery intakes on 23 May was 17.8°C from the surface to a depth of 3 m and declined with increasing depth to 12.8°C at 8 m near the bottom of the headpond (Fig. 1). Dissolved oxygen concentration at the surface on that date was 7.9 mg/L similar to the concentrations measured at all depths of the headpond. Free carbon dioxide concentration was about 3.6 mg/L from the surface to a depth of 5 m and increased to 6.5 mg/L at 8 m. A similar pattern of change in temperature and the concentrations of oxygen and carbon dioxide was apparent from the surface of the headpond to the bottom on 20 June except that oxygen near the bottom had decreased to 6.5 mg/L. By 18 July, there had been a further decrease in oxygen concentration near the bottom of the headpond to 5.9 mg/L.

Temperature on 22 August was 24.0°C from the surface of the headpond to a depth of 4 m and declined to 20.2°C at 8 m (Fig. 1). Oxygen concentration on that date measured 8.2 mg/L from the surface to a depth of 4 m and declined to 1.7 mg/L at 8 m. Carbon dioxide concentration at a depth of 8 m was 11.2 mg/L on that date. Thermal stratification was no longer apparent on 19 September when temperature measured 19°C from the surface of the headpond to the bottom. Oxygen concentration near the bottom had increased to 5.7 mg/L by that date and carbon dioxide concentration had decreased to 4.8 mg/L. Temperature had declined further by 22 October and measured 10°C from the surface of the headpond to the bottom. Dissolved oxygen concentration was 10.5 mg/L and carbon dioxide concentration 2.5 mg/L at all depths of the headpond on that date.

Concentrations of iron (260 µg/L), manganese (60 µg/L) and aluminum (120 µg/L) did not change from the surface of the headpond to the bottom on 23 May (Fig. 2). Similarly, concentrations of manganese (60 µg/L) and aluminum (260 µg/L) remained constant from the surface of the headpond to the bottom on 20 June and on all subsequent sampling dates. Iron concentration was 340 µg/L from the surface to 7 m on 20 June and increased to 680 µg/L at 8 m. Similar concentrations of iron were measured at various depths of the headpond on 18 July. The concentration of iron at the surface on 22 August was 280 µg/L, 400 µg/L at 5 m and 1520 µg/L at 8 m. This relatively high concentration of iron near the bottom of the headpond occurred when oxygen concentration in that area had decreased to 1.7 mg/L and when carbon dioxide had increased to 11.2 mg/L. The headpond was no longer thermally stratified on 19 September

when iron concentration near the bottom had decreased to 560 µg/L. By 22 October, iron measured 300 µg/L from the surface of the headpond to the bottom.

There was no change in pH from the surface of the headpond to the bottom on the various sampling dates (Table 1). There was, however, a gradual increase in the pH of the headpond during the 23 May - 22 August period. For example, pH at a depth of 8 m increased from 5.06 to 5.39 during that period. Values of pH on 19 September and 22 October were similar to those observed on 22 August.

Concentrations of total ammonia on the various sampling dates were within the <0.01 - 0.11 mg/L range from the surface to a depth of 7 m and increased to within the 0.05 - 0.44 mg/L range at 8 m near the bottom of the headpond (Table 2).

Apparent colour on the various sampling dates was similar from the surface of the headpond to a depth of 6 m and increased near the bottom at depths of 7 and 8 m (Table 3). The increase in the apparent colour of the water near the bottom of the headpond was most pronounced on 22 August. For example, colour measured 55 relative units from the surface to a depth of 5 m on that date and 110 units at 8 m. The headpond was no longer thermally stratified on 22 October when apparent colour was 50 relative units from the surface to the bottom.

DISCUSSION

Iron can be bi-valent or tri-valent as the ferrous or ferric form. The ferrous form exists only in the absence of oxygen and the ferric form is insoluble (Ruttner 1963). Ruttner (1963) has concluded that water can dissolve greater amounts of iron as ferrous bicarbonate when it is nearly free of dissolved oxygen, when it contains adequate amounts of free carbon dioxide, when the pH is not above 7.5 and when organic substances arising from decomposition are present to reduce ferric hydroxide. Redox potentials of 0.4 - 0.6 volt observed in epilimnetic lake water are lower in the hypolimnion because of reducing substances derived from the mud (Hutchinson 1957). In the hypolimnia of lakes where the redox potential is less than 0.3 volt, ferrous iron may be expected to occur (Hutchinson 1957). Iron is reduced in the mineral fraction of suspended particles and in the bottom sediments where redox potentials vary around 0.0 volt and dissolved as ferrous bicarbonate. Generally, in holomictic lakes where the oxygen curve is orthograde, iron content varies little vertically (Hutchinson 1957). However, in lakes where there is a clinograde oxygen curve, an inverse relationship between iron and oxygen is normally well developed.

The oxygen curve in the Big Falls headpond was orthograde during May 1989. However, during June and July of that year, there was a detectable decrease in dissolved oxygen concentration near the bottom of the headpond and by 22 August a clinograde oxygen curve had developed. Thus, oxygen concentration in the upper 4 m of the headpond on 22 August was 8.2 mg/L but declined to 1.7 mg/L near the bottom. The decline in oxygen concentration at the bottom of the headpond was accompanied by an increase in the concentration of free carbon dioxide to 11.2 mg/L, considerably greater than the concentration of 2.4 mg/L measured in the epilimnion. Apparent colour was 55 relative units in the upper 5 m of the headpond on that date and increased to 110 units near the bottom where pH was 5.39. Conditions at the bottom of the headpond during August appear to have been favourable for the reduction of ferric iron in the bottom sediments and the subsequent release of soluble ferrous iron. Accordingly, total iron near the bottom of the headpond measured 320 µg/L on 23 May, had increased to 770 µg/L on 18 July and reached a peak of 1520 µg/L on 22 August. No unusual mortality of salmon parr occurred during August 1989 nor was ferric hydroxide observed in the rearing

ponds. Concentrations of total iron near the bottom of the headpond the previous year, which were associated with the mortality of salmon parr, ranged from 4010-4405 µg/L and occurred when oxygen concentration had declined to 0.2 mg/L.

The Canadian Water Quality Guidelines (1987) indicate that, for the protection of freshwater aquatic life, the concentration of total iron should not exceed 300 µg/L. It is apparent that concentrations of iron not harmful to aquatic life in the Mersey River can be considerably greater than 300 µg/L. Relatively high concentrations of iron are found in brown waters such as those of the Mersey River because the humic acids present form colloidally dissolved humates with iron (Ruttner 1963). These organic iron sols are more stable than the inorganic bicarbonate solutions and humic waters usually contain considerable amounts of iron in the presence of oxygen. For example, on 22 October during the autumnal circulation, oxygen measured 10.4 mg/L from the surface of the Big Falls headpond to the bottom and iron 300 µg/L.

There was a marked increase in the apparent colour of the water at the bottom of the Big Falls headpond during August when a value of 110 relative units was observed. Colour at the bottom of the headpond the previous year when mortality of the salmon occurred was 220 relative units. Hutchinson (1957) indicates that, early in the period of thermal stratification before ferrous iron is detectable, there can be a considerable increase in the total iron concentration of the hypolimnetic water. The increase in iron is accompanied by an increase in colour, which is attributable to the simultaneous diffusion of ferrous iron from the reduced mud surface and the downward turbulent movement of oxygen from above. The ferrous iron is therefore oxidized as it enters the water producing a temporary ferric oxide sol (Hutchinson 1957). This may in part sediment but will later be reduced so that at the end of stratification all of the iron will be present in di-valent form. Yoshimura (1932 cited in Hutchinson 1957) has indicated that if ferrous bicarbonate is present near the bottom of a lake, the hypolimnion may be buffered so that the pH curve is altered. However, pH did not change from the surface to the bottom of the Big Falls headpond on 22 August 1989, suggesting that the increased concentration of iron measured near the bottom on that occasion may have been present as a ferric oxide sol.

The Big Falls headpond had cooled to 19°C by 19 September and thermal stratification was no longer apparent. This allowed circulation within the headpond and resulted in an increased oxygen concentration of 5.7 mg/L near the bottom and decreased concentrations of free carbon dioxide and total iron of 4.8 mg/L and 560 µg/L, respectively. Circulation was complete by 22 October when no change in temperature or in the concentrations of oxygen (10.4 mg/L), carbon dioxide (2.5 mg/L) or total iron (300 µg/L) were observed from the surface of the headpond to the bottom.

There was no appreciable increase in the concentrations of manganese or aluminum near the bottom of the headpond during August 1989 as observed for iron. All concentrations of total aluminum measured during this study (range 60-326 µg/L) exceeded the Canadian Water Quality Guideline (1987) of 5 µg/L total aluminum for waters with pH equal to or below 6.5. However, these concentrations of total aluminum were no greater than concentrations which have been recorded for other brown, acidic rivers in Nova Scotia (Lacroix and Townsend 1987; Farmer et al. 1988). Lacroix and Townsend (1987) have shown that concentrations of toxic, inorganic aluminum in these rivers represent less than 10% of the total dissolved aluminum present and that this metal is not associated with mortality of juvenile salmon.

Un-ionized ammonia can be toxic to fish. That portion of the total ammonia concentration present in the un-ionized form is dependent upon pH and temperature. By comparing the recommended guidelines for total ammonia (Canadian Water Quality Guidelines 1987) and the concentrations measured in

the Big Falls headpond, it is evident that concentrations of un-ionized ammonia present during this study were not harmful to the salmon.

Hydrogen sulphide was present near the bottom of the Big Falls headpond during August 1988 when mortality of the salmon parr occurred (Farmer et al. 1989b) but not during the present study. The bacterial reduction of sulphate and the decomposition of organic sulphur compounds both result in the production of hydrogen sulphide (Hutchinson 1957). The reduction of sulphate and the appearance of H_2S occurs at a lower redox potential than that at which ferrous iron appears in quantity (Hutchinson 1957). Thus, considerable ferrous iron can enter the water from the surface layer of mud before hydrogen sulphide is produced. Since ferrous sulphide is relatively insoluble, the final stages of stagnation can sometimes be marked by a loss of ferrous iron from the deep water . The precipitation of ferrous sulphide in the presence of hydrogen sulphide will only occur when there is an alkaline reaction (Ruttner 1963).

Caution is required when the hypolimnetic water of headponds or lakes is withdrawn for fish culture purposes. Oxygen depletion of the hypolimnion can result from the enzymatic and bacterial breakdown of organic matter and from the respiration of organisms. This can result in the reduction of ferric hydroxide in the bottom sediments and the release of soluble ferrous iron. Oxygenation of water containing ferrous iron can result in the formation of ferric hydroxide, an insoluble precipitate, which can cause the respiratory impairment of cultured fish. The use of an alternate hatchery intake for withdrawal of oxygenated water from the epilimnion or metalimnion is required if the hypolimnion is known to become anoxic.

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Table 1. Values of pH at various depths of the Big Falls headpond during the 23 May - 22 October period, 1989.

	Date					
Depth,m	23 May	20 Jun	18 Jul	22 Aug	19 Sep	22 Oct
0	5.16	5.22	5.30	5.46	5.43	5.43
1	5.16	5.22	5.31	5.45	5.40	5.42
2	5.17	5.20	5.31	5.48	5.40	5.40
3	5.13	5.17	5.30	5.46	5.40	5.41
4	5.13	5.18	5.30	5.48	5.40	5.40
5	5.13	5.17	5.31	5.39	5.43	5.42
6	5.06	5.17	5.38	5.32	5.40	5.34
7	5.06	5.17	5.26	5.34	5.42	5.43
8	5.06	5.19	5.28	5.39	5.38	5.43

Table 2. Total ammonia concentration (mg/L) at various depths of the Big Falls headpond during the 20 June - 22 October period, 1989.

	Date				
Depth,m	20 Jun	18 Jul	22 Aug	19 Sep	22 Oct
0	<0.01	0.02	0.01	0.03	0.02
3	<0.01	0.02	0.05	0.03	0.02
5	<0.01	0.02	0.01	0.03	0.02
6					0.02
7	0.02	0.03	0.06	0.11	0.02
8	0.44	0.17	0.10	0.05	0.09

Table 3. Apparent colour (relative units) at various depths of the Big Falls headpond during the 23 May - 22 October period, 1989.

	Date					
Depth,m	23 May	20 Jun	18 Jul	22 Aug	19 Sep	22 Oct
0	65	65	55	55	50	50
1	65	65	55	55	50	50
2	65	65	55	55	50	50
3	65	65	55	55	50	50
4	65	65	55	55	50	50
5	65	65	55	55	50	50
6	65	65	55	65	50	50
7	70	65	65	75	50	50
8	70	70	65	110	65	50

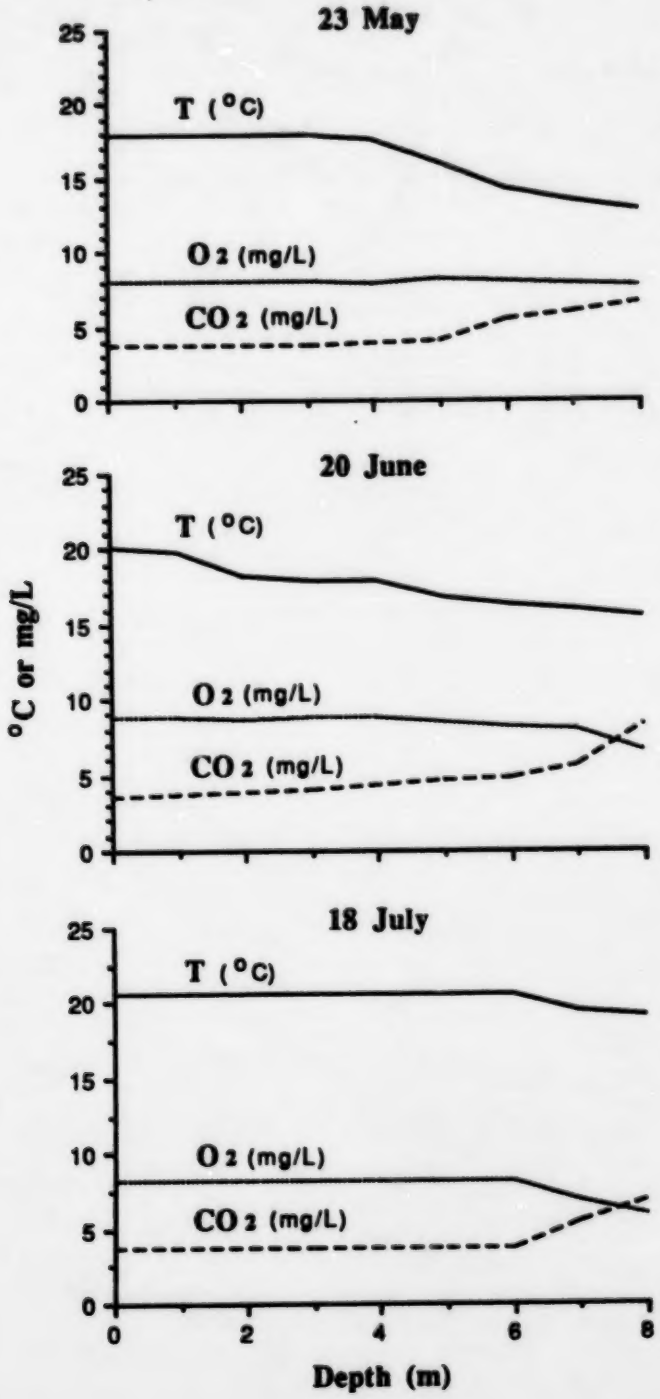
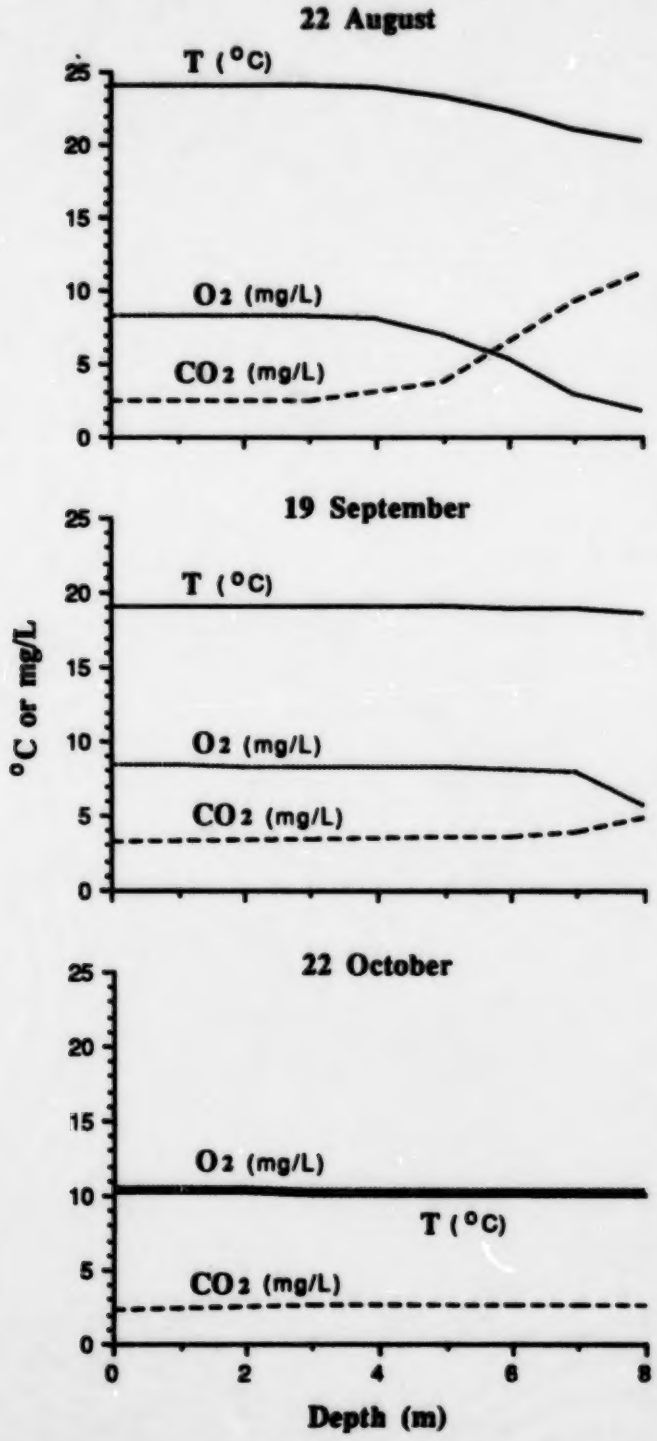


FIGURE 1. Temperature, dissolved oxygen and free carbon dioxide concentrations at various depths of the Big Falls headpond during the 23 May - 22 October period, 1989.


22 August
T (°C)
O2 (mg/L)
CO2 (mg/L)
19 September
T (°C)
O2 (mg/L)
CO2 (mg/L)
22 October
O2 (mg/L)
T (°C)
CO2 (mg/L)
°C or mg/L
Depth (m)
0
5
10
15
20
25
0
2
4
6
8

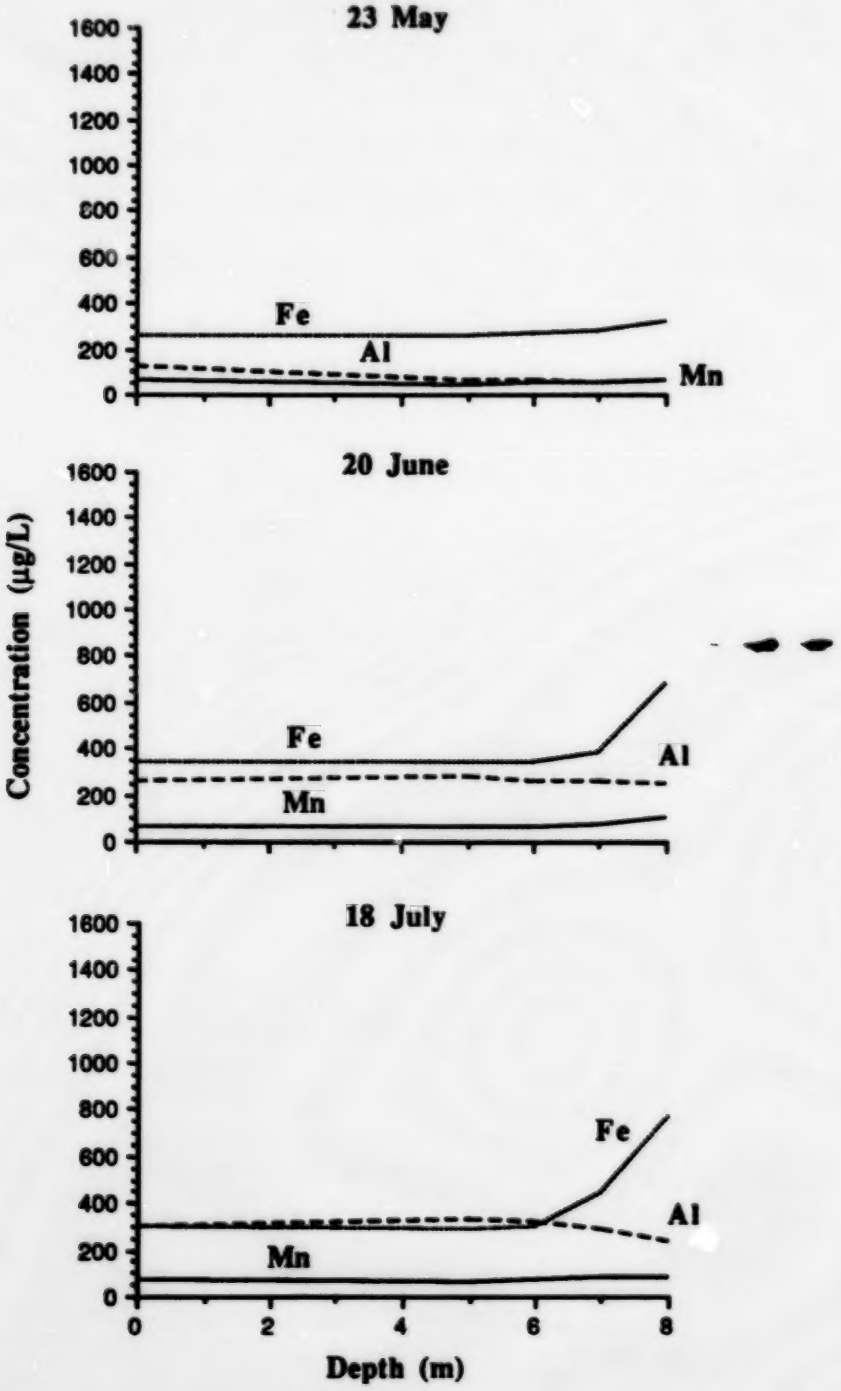
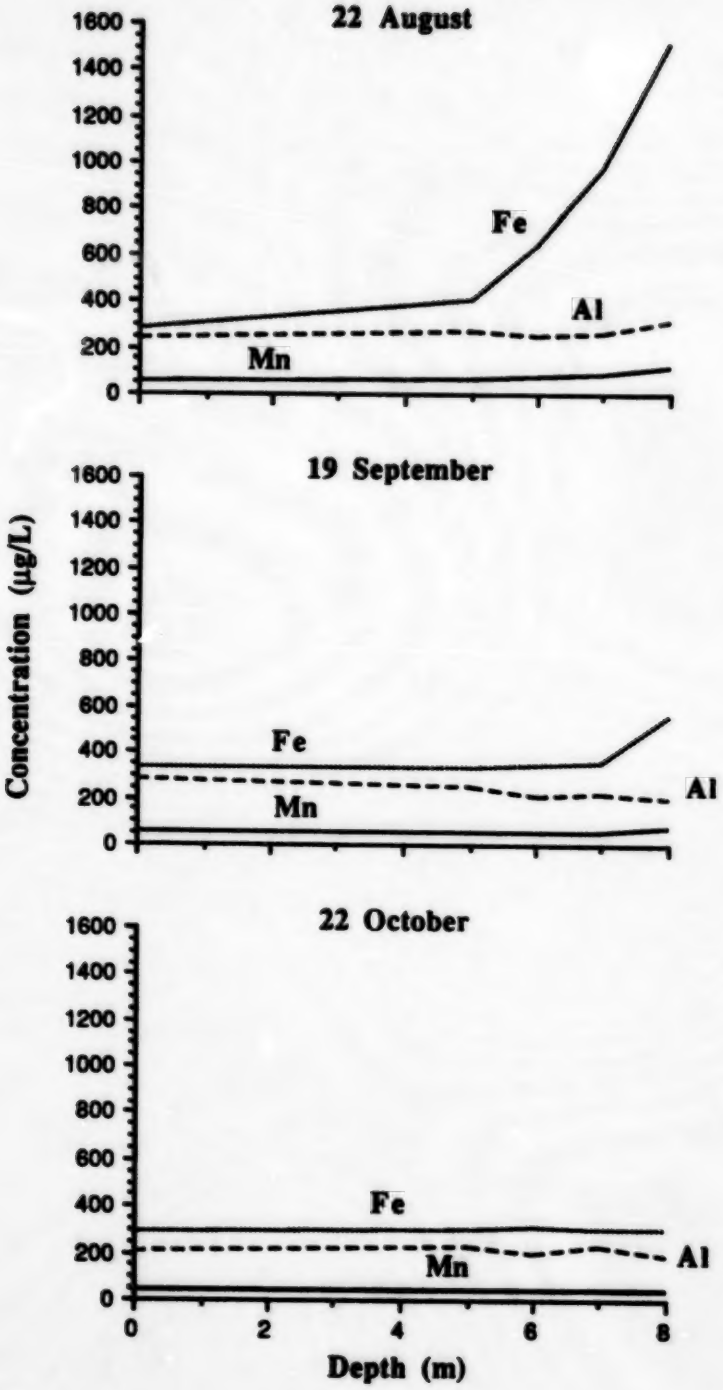


FIGURE 2. Iron, aluminum and manganese concentrations at various depths of the Big Falls headpond during the 23 May - 22 October period, 1989.


22 August
1600
1400
1200
1000
800
600
400
200
0
Fe
Al
Mn
19 September
Concentration (µg/L)
Fe
Al
Mn
22 October
Fe
Al
Mn
0
2
4
6
8
Depth (m)